AAPCO

PESTICIDE FORMULATIONS CHECK SAMPLE PROGRAM

2016

REPORT

April 5, 2016

Office of Indiana State Chemist
Purdue University
175 S. University Street
West Lafayette, IN 47907

April 5, 2016

Dear AAPCO Check Sample participants,

The final report of the 2016 Pesticide Formulation Check Sample Program is enclosed and will also be posted on the AAPCO website, Laboratory Issues section.

The 2016 sample set was a typical selection of commercial products consisting of three formulated products with four pesticide active ingredients. Most laboratories reported data for all four analytes, giving good data sets for statistical analysis. To ensure a high quality for the test materials offered, homogeneity of all samples offered were evaluated by the hosting laboratory; please see these results summarized in Table 1.

Data has been analyzed for the individual method type used. We have been using the modified Z-score test for outlier identification since 2006. Comparing to the traditional Dixon's and Grubb's outlier tests, the modified Z-score test is less prone to extreme values, since it is based on the median rather than the mean, which can sometimes be skewed by the extreme values. Please refer to the Appendix for references of the statistical analysis applies. If there are more than one major analytical technique involved (e.g. HPLC and GC), separate tests based on an outlier resistant estimator i.e. the median of absolute deviation about the median (MAD) were run to reveal the outliers in each data set produced by the same method type. After the removal of outliers, a 1-sided t-test of the remaining data was performed to reveal if there is any significant difference between different method types. When the t-test revealed no significant difference among the methods used, data collected from all method types were charted together. The charts also graph the allowed deviations passed upon the label claim using AAPCO adopted Horwitz limits. Error bars were incorporated in the chart to express the degree of uncertainty of each lab's measurement. If you have any questions regarding how data were processed statistically, please contact me.

I would like to hear from you any suggestions you might have for future active ingredients and sample selections for the program. Ideally, we would like to include samples, all active ingredients of which can be analyzed by each lab, so that the most useful data groups for statistical analysis can be generated. I have in mind some products for next year's program; herbicides and insecticides will continue to be offered, as well as a product of fungicide of your choice.

Last but not least, I would like to thank my staff, Dr. Jianming Lei, Ms. Natalie Wilson, and Dr. Nayane Udawatte from the Indiana State Chemist Office, for their extraordinary efforts in preparing the sample sets, conducting homogeneity tests, performing statistical analysis, and putting together the report.

Thank you all very much for your continued support. I hope you find the program and the enclosed report useful and I look forward to working with you in another exciting year.

Sincerely,

Mrs. Ping Wan
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Table 1A: Summary of participation per active ingredient

AAPCO Check Sample #	Product Description	Active Ingredient	# of Participating Labs	# of Labs using GC	# of Labs using LC	Significant difference between LC and GC[1]?	Percent of results failing the sample[2]?
2016-1	Opaque White Liquid	2,4-D, Acid Equivalent	62	16	46	No	17%
		2,4-D, Ester Form	16	16	0	N/A	6%
2016-2	Transparent Amber Liquid	Glyphosate	74	0	74	N/A	8%
2016-3	Granular	Imidacloprid	73	2	71	N/A	15%
		Lambda-Cyhalothrin	67	47	20	No	10%

Table 1B: Summary of lab results per active ingredient, including outliers

AAPCO Check Sample #	Analyte and Label Claim	Minimum Result	Maximum Result	Grand Average	Grand %CV	Homogeneity Test Results Average	Homogeneity Test Results %CV[3]
2016-1	2,4-D, Acid Equivalent (41.5%)	21.10	48.44	40.46	9.87	39.94	2.5
	2,4-D, Ester Form (62.6%)	56.10	66.00	62.11	3.72	n/a	n/a
2016-2	Glyphosate, Acid Equivalent (30.38%)	18.92	38.42	30.81	7.13	30.86	1.6
2016-3	Imidacloprid (0.5%)	0.280	0.673	0.478	15.18	0.487	6.6
	Lambda-Cyhalothrin (0.1%)	0.074	0.198	0.105	24.41	0.095	5.8

Table 1C: Summary of lab results per active ingredient, excluding outliers

AAPCO Check Sample #	Analyte and Label Claim	# of Outliers[4]	Average Excluding Outliers	%CV Excluding Outliers	Homogeneity Test Results Average	Homogeneity Test Results %CV[3]
2016-1	2,4-D, Acid Equivalent (41.5%)	10	41.56	2.87	39.94	2.5
	2,4-D, Ester Form (62.6%)	1	62.48	2.84	n/a	n/a
2016-2	Glyphosate, Acid Equivalent (30.38%)	5	30.77	3.21	30.86	1.6
2016-3	Imidacloprid (0.5%)	0	0.478	15.18	0.487	6.6
	Lambda-Cyhalothrin (0.1%)	7	0.097	11.13	0.095	5.8

[1] Determined by Welch's *t*-test
[2] Where failing indicates a mean assay result outside the Horwitz defined acceptable limits
[3] Homogeneity tests were performed by the host laboratory prior to shipping samples to participating labs. Ten subsamples were randomly selected and tested
[4] An Outlier is flagged when the modified Z-score falls outside the range of $-3.5 \leq Z_i \leq 3.5$; see Appendix for calculations

Table 2: Summary results for AAPCO Check Sample 2016-1, 2,4-D. AAPCO Check sample 2016-1 is an opaque white liquid with a claim of 41.5% 2,4-D, Acid Equivalent

Lab #	Method	2-Day Average[1]	RPD[1]	Modified Z Score[2]	Outlier[2]
2	GC-FID	42.306	0.50	0.707	NO
3	LC-UV	37.975	0.39	-2.949	NO
5	GC-FID	40.881	0.00	-0.496	NO
6	LC-UV	42.150	2.14	0.576	NO
8	GC-FID	43.758	2.12	1.933	NO
9	GC-FID	41.438	0.32	-0.026	NO
10	LC-MSD	37.200	3.23	-3.604	YES
14	GC-FID	40.734	2.97	-0.620	NO
15	GC-FID	39.339	0.79	-1.798	NO
16	LC-UV	33.900	1.77	-6.390	YES
17	GC-MSD	37.194	0.04	-3.608	YES
18	LC-UV	41.480	0.43	0.010	NO
20	LC-UV	48.435	5.26	5.882	YES
21	LC-UV	40.017	0.54	-1.225	NO
22	LC-UV	37.063	0.26	-3.719	YES
23	LC-UV	39.472	3.54	-1.686	NO
24	LC-UV	43.150	0.23	1.420	NO
25	LC-UV	21.095	4.03	-17.201	YES
27	LC-UV	33.127	2.54	-7.043	YES
29	LC-UV	40.403	2.15	-0.899	NO
32	GC-FID	41.670	1.43	0.170	NO
35	LC-UV	44.023	3.01	2.157	NO
36	GC-FID	43.029	2.47	1.317	NO
37	LC-UV	36.150	0.83	-4.490	YES
38	LC-UV	41.850	0.24	0.322	NO
39	LC-UV	43.025	5.18	1.314	NO
40	LC-UV	39.940	1.43	-1.291	NO
41	GC-FID	41.471	1.12	0.002	NO
42	LC-UV	41.445	0.41	-0.020	NO
44	GC-MSD	41.338	10.10	-0.110	NO
45	LC-UV	42.432	0.31	0.814	NO
47	LC-UV	40.720	0.83	-0.632	NO
50	GC-FID	40.708	0.33	-0.642	NO
53	GC-FID	41.000	0.81	-0.395	NO
54	GC-FID	39.250	1.01	-1.873	NO
58 GC	GC-FID	42.508	0.32	0.878	NO
58 LC	LC-UV	41.350	1.69	-0.100	NO
59	LC-UV	41.577	0.10	0.091	NO
63	LC-UV	42.565	0.00	0.926	NO
67	LC-UV	41.875	0.45	0.343	NO
68	LC-UV	42.080	0.33	0.516	NO
70	LC-UV	42.035	1.50	0.478	NO
71	LC-UV	44.100	0.00	2.222	NO
73	LC-UV	41.466	0.09	-0.002	NO
74	LC-UV	41.950	0.24	0.407	NO
76	LC-UV	24.450	10.22	-14.368	YES
77	LC-UV	42.197	0.67	0.615	NO
78	LC-UV	41.670	1.11	0.170	NO
79	LC-UV	35.970	1.56	-4.642	YES
80	LC-UV	41.550	0.24	0.069	NO
82	LC-UV	42.100	0.95	0.533	NO
83	LC-UV	42.411	0.84	0.796	NO
85	GC-FID	41.537	0.80	0.058	NO
87	GC-FID	41.859	0.05	0.329	NO
88	LC-UV	41.115	0.02	-0.298	NO
91	LC-UV	42.470	0.54	0.845	NO
94	LC-UV	41.050	1.22	-0.353	NO
96	LC-UV	41.772	2.24	0.257	NO
97	LC-UV	43.409	5.02	1.638	NO
99	LC-UV	40.054	1.02	-1.194	NO
102	LC-UV	40.387	0.18	-0.913	NO
103	LC-UV	41.700	2.88	0.196	NO
104	LC-UV	41.305	0.32	-0.138	NO
106	LC-UV	41.438	0.32	-0.026	NO

Lower Horwitz[3]	38.658
Upper Horwitz[3]	47.185
Grand Average[4]	40.455
Total SD[4]	3.994
Total Median[4]	41.468
MAD_E[5]	1.185

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified *Z*-score falls outside the range of $-3.5 \leq Z_i \leq 3.5$; see Appendix.
[3] Based on AAPCO adopted Allowed Deviations of Analytical Results from Label Claims, i.e. Horwitz limits for uniform samples based on median yield.
[4] Grand average, standard deviation, and median.
[5] Median Absolute Deviation Robust estimate of standard deviation; see Appendix for calculations.

Table 3: Summary results for AAPCO Check Sample 2016-1, 2,4-D. AAPCO Check sample 2016-1 is an opaque white liquid with a claim of 62.6% 2,4-D in Isooctyl (2-ethylhexyl) ester form.

Lab #	Method	2-Day Average[1]	RPD[1]	Modified Z Score[2]	Outlier[2]
2	GC-FID	63.810	0.50	0.833	NO
5	GC-FID	61.660	0.00	-0.534	NO
8	GC-FID	66.000	2.12	2.226	NO
9	GC-FID	62.500	0.32	0.000	NO
14	GC-FID	61.440	2.97	-0.675	NO
15	GC-FID	59.335	0.79	-2.013	NO
17	GC-MSD	56.100	0.04	-4.071	YES
32	GC-FID	62.850	1.43	0.223	NO
36	GC-FID	64.900	2.47	1.526	NO
41	GC-FID	62.550	1.12	0.032	NO
44	GC-MSD	62.350	10.10	-0.095	NO
50	GC-FID	61.400	0.33	-0.700	NO
53	GC-FID	61.840	0.81	-0.420	NO
54	GC-FID	59.200	1.01	-2.099	NO
58 GC	GC-FID	64.115	0.32	1.027	NO
85	GC-FID	62.650	0.80	0.095	NO
87	GC-FID	63.135	0.05	0.404	NO

Lower Horwitz[3]	58.570
Upper Horwitz[3]	70.661
Grand Average[4]	62.108
Total SD[4]	2.313
Total Median[4]	62.500
MAD_E[5]	1.573

1 Average yield and Relative Percent Difference between the two-day determinations per laboratory.
2 An outlier is flagged when the modified *Z*-score falls outside the range of $-3.5 \leq Z_i \leq 3.5$; see Appendix.
3 Based on AAPCO adopted Allowed Deviations of Analytical Results from Label Claims, i.e. Horwitz limits for uniform samples based on median yield.
4 Grand average, standard deviation, and median.
5 Median Absolute Deviation Robust estimate of standard deviation; see Appendix for calculations.

Note: 2,4-D can be analyzed in either its ester form via GC or the acid equivalent after a saponification procedure. Data submitted using GC technique was graphed to demonstrate results in ester form. Those results were then converted into the acid form, via a factor of 0.663 for the conversion of isooctyl (2-ethylhexyl) ester, and all results were graphed together. For example, 63.810% 2,4-D isooctyl (2-ethylhexyl) ester is equivalent to 42.306% 2,4-D acid equivalent.

Table 4: Summary results for AAPCO Check Sample 2016-2, Glyphosate. AAPCO Check sample 2016-2 is a transparent amber liquid with a claim of 30.38% Glyphosate, Acid Equivalent.

Lab #	Method	2-Day Average[1]	RPD[1]	Modified Z Score[2]	Outlier[2]
1	LC-MSD	26.528	2.34	-4.391	YES
2	LC-UV	31.775	0.54	1.160	NO
3	LC-UV	31.815	0.53	1.202	NO
5	LC-UV	34.968	1.05	4.538	YES
6	LC-UV	31.150	0.96	0.499	NO
8	LC-UV	31.302	3.34	0.660	NO
9	LC-UV	30.540	1.05	-0.147	NO
10	LC-MSD	31.550	10.46	0.922	NO
14	LC-UV	30.262	0.02	-0.441	NO
15	LC-UV	28.355	1.38	-2.458	NO
16	LC-UV	27.850	9.69	-2.993	NO
17	LC-FLD	32.625	0.58	2.059	NO
18	LC-UV	31.200	0.77	0.552	NO
20	LC-UV	31.775	4.31	1.160	NO
21	LC-UV	29.319	0.53	-1.438	NO
22	LC-UV	30.865	0.42	0.197	NO
23	LC-UV	38.715	1.73	8.503	YES
24	LC-UV	30.700	0.00	0.023	NO
25	LC-UV	18.915	5.45	-12.446	YES
27	LC-UV	29.670	0.07	-1.067	NO
29	LC-UV	30.800	0.65	0.129	NO
31	LC-UV	31.330	1.02	0.689	NO
32	LC-UV	31.350	0.32	0.710	NO
35	LC-UV	29.785	1.51	-0.945	NO
36	LC-MSD	29.000	0.69	-1.776	NO
37	LC-UV	31.100	0.64	0.446	NO
38	LC-UV	30.550	0.33	-0.136	NO
39	LC-UV	31.260	8.13	0.615	NO
40	LC-UV	30.860	0.72	0.192	NO
41	LC-UV	30.100	6.64	-0.612	NO
42	LC-UV	31.960	3.19	1.356	NO
44	LC-MSD	37.600	2.13	7.323	YES
45	LC-UV	30.950	1.62	0.287	NO
47	LC-UV	32.020	1.37	1.419	NO
50	LC-UV	30.350	0.33	-0.348	NO
53	LC-UV	31.155	0.74	0.504	NO
54	LC-UV	29.900	2.01	-0.824	NO
56	LC-UV	30.176	0.97	-0.532	NO
58	LC-UV	31.350	0.96	0.710	NO
59	LC-UV	30.321	0.26	-0.379	NO
63	LC-UV	29.800	0.00	-0.929	NO
66	LC-UV	30.625	0.42	-0.057	NO
67	LC-MSD	30.235	0.63	-0.469	NO
68	LC-UV	30.610	0.46	-0.072	NO
70	LC-UV	30.480	2.30	-0.210	NO
71	LC-UV	30.152	0.00	-0.557	NO
73	LC-UV	30.872	0.77	0.204	NO
74	LC-UV	31.750	2.20	1.134	NO
76	LC-UV	30.485	1.08	-0.205	NO
77	LC-UV	30.697	0.74	0.019	NO
78	LC-UV	30.600	1.31	-0.083	NO
79	LC-UV	33.390	0.90	2.869	NO
80	LC-UV	30.100	1.33	-0.612	NO
81	LC-UV	30.580	6.01	-0.105	NO
82	LC-UV	30.700	0.65	0.023	NO
83	LC-UV	31.923	0.04	1.317	NO
85	LC-UV	29.930	3.44	-0.792	NO
86	LC-UV	30.150	1.66	-0.559	NO
87	LC-UV	30.310	0.73	-0.390	NO
88	LC-UV	30.460	0.33	-0.231	NO
89	LC-UV	30.661	0.93	-0.019	NO
90	LC-UV	29.340	2.32	-1.416	NO
91	LC-UV	32.175	1.37	1.583	NO
94	LC-UV	29.800	3.36	-0.929	NO
95	LC-UV	30.240	0.13	-0.464	NO
96	LC-UV	31.670	1.26	1.049	NO
97	LC-UV	31.374	2.17	0.736	NO
99	LC-UV	32.211	2.61	1.621	NO
102	LC-MSD	32.240	0.19	1.652	NO
103	LC-UV	30.335	0.63	-0.363	NO
104	LC-UV	32.750	6.41	2.192	NO
105	LC-UV	30.396	0.41	-0.299	NO
109	LC-UV	29.650	1.01	-1.088	NO
110	LC-UV	31.663	0.84	1.041	NO

Lower Horwitz[3]	28.199
Upper Horwitz[3]	34.742
Grand Average[4]	30.813
Total SD[4]	2.196
Total Median[4]	30.679
MAD_E[5]	0.946

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified Z-score falls outside the range of $-3.5 \leq Zi \leq 3.5$; see Appendix.
[3] Based on AAPCO adopted Allowed Deviations of Analytical Results from Label Claims, i.e. Horwitz limits for uniform samples based on median yield.
[4] Grand average, standard deviation, and median.
[5] Median Absolute Deviation Robust estimate of standard deviation; see Appendix for calculations.

Table 5: Summary results for AAPCO Check Sample 2016-3, Imidacloprid. AAPCO Check Sample 2016-3 is a granular sample with a claim of 0.5% Imidacloprid.

Lab #	Method	2-Day Average[1]	RPD[1]	Modified Z Score[2]	Outlier[2]
1	LC-MSD	0.429	4.22	-0.823	NO
2	LC-UV	0.440	4.32	-0.658	NO
3	LC-UV	0.425	11.76	-0.894	NO
5	LC-UV	0.460	0.00	-0.325	NO
6	LC-UV	0.496	4.24	0.252	NO
8	LC-UV	0.485	28.69	0.073	NO
9	LC-UV	0.415	2.41	-1.056	NO
10	LC-MSD	0.529	3.97	0.788	NO
14	LC-UV	0.515	12.04	0.569	NO
15	LC-UV	0.480	12.50	0.000	NO
16	LC-UV	0.335	2.99	-2.357	NO
17	LC-MSD	0.525	3.47	0.723	NO
18	LC-UV	0.466	3.65	-0.236	NO
19	LC-UV	0.514	0.39	0.553	NO
20	LC-UV	0.511	12.13	0.504	NO
21	LC-UV	0.346	1.45	-2.186	NO
22	LC-UV	0.673	0.71	3.138	NO
23	LC-UV	0.555	10.09	1.219	NO
24	LC-UV	0.407	4.18	-1.195	NO
25	LC-UV	0.520	11.54	0.650	NO
27	LC-UV	0.540	1.48	0.975	NO
29	LC-UV	0.540	38.00	0.967	NO
31	LC-UV	0.442	5.21	-0.626	NO
32	LC-UV	0.488	0.00	0.130	NO
35	LC-UV	0.470	0.00	-0.163	NO
36	LC-MSD	0.508	1.97	0.455	NO
37	LC-UV	0.404	0.50	-1.235	NO
38	LC-UV	0.413	3.15	-1.097	NO
39	LC-UV	0.504	9.73	0.382	NO
40	LC-UV	0.487	1.64	0.114	NO
41	LC-UV	0.427	12.43	-0.870	NO
42	GC-FID	0.439	2.28	-0.666	NO
44	LC-MSD	0.390	7.45	-1.471	NO
45	LC-UV	0.403	3.23	-1.260	NO
47	LC-UV	0.489	10.22	0.146	NO
50	LC-UV	0.439	3.88	-0.675	NO
53	GC-FID	0.430	13.95	-0.813	NO
54	LC-UV	0.492	7.12	0.187	NO
56	LC-UV	0.648	2.34	2.735	NO
58	LC-UV	0.515	0.58	0.561	NO
59	LC-UV	0.467	2.57	-0.211	NO
63	LC-UV	0.280	0.00	-3.251	NO
67	LC-MSD	0.472	0.85	-0.130	NO
68	LC-UV	0.535	4.30	0.886	NO
70	LC-UV	0.545	9.17	1.056	NO
71	LC-UV	0.641	0.00	2.612	NO
73	LC-UV	0.442	1.36	-0.618	NO
74	LC-UV	0.457	4.16	-0.382	NO
76	LC-UV	0.430	0.00	-0.813	NO
77	LC-UV	0.447	3.13	-0.536	NO
78	LC-UV	0.410	4.88	-1.138	NO
79	LC-UV	0.476	7.75	-0.064	NO
80	LC-UV	0.510	7.84	0.488	NO
81	LC-UV	0.505	1.98	0.406	NO
83	LC-UV	0.407	36.36	-1.186	NO
85	LC-UV	0.429	6.06	-0.829	NO
87	LC-UV	0.464	1.08	-0.265	NO
88	LC-MSD	0.530	3.77	0.813	NO
89	LC-UV	0.590	2.88	1.780	NO
90	LC-UV	0.319	0.31	-2.612	NO
91	LC-UV	0.502	0.70	0.362	NO
94	LC-UV	0.549	4.56	1.113	NO
96	LC-UV	0.480	15.00	0.000	NO
97	LC-UV	0.471	17.64	-0.154	NO
99	LC-UV	0.505	4.96	0.398	NO
100	LC-UV	0.430	2.74	-0.808	NO
102	LC-UV	0.636	0.16	2.527	NO
103	LC-UV	0.504	0.60	0.382	NO
104	LC-UV	0.540	3.70	0.975	NO
106	LC-UV	0.504	6.55	0.382	NO
107	LC-UV	0.492	5.28	0.195	NO
109	LC-UV	0.578	18.18	1.585	NO
110	LC-UV	0.352	2.27	-2.080	NO

Lower Horwitz[3]	0.4112
Upper Horwitz[3]	0.6776
Grand Average[4]	0.478
Total SD[4]	0.073
Total Median[4]	0.480
MAD_E[5]	0.062

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified Z-score falls outside the range of $-3.5 \leq Zi \leq 3.5$; see Appendix.
[3] Based on AAPCO adopted Allowed Deviations of Analytical Results from Label Claims, i.e. Horwitz limits for uniform samples based on median yield.
[4] Grand average, standard deviation, and median.
[5] Median Absolute Deviation Robust estimate of standard deviation; see Appendix for calculations.

Table 6: Summary results for AAPCO Check Sample 2016-3, Lambda-Cyhalothrin. AAPCO Check sample 2016-3 is a granular sample with a claim of 0.1% Lambda-Cyhalothrin.

Lab #	Method	2-Day Average[1]	RPD[1]	Modified Z Score[2]	Outlier[2]
1	GC-MSD	0.0886	6.095	-0.631	NO
2	LC-UV	0.1004	9.163	0.403	NO
3	GC-FID	0.1020	5.882	0.543	NO
5	GC-FID	0.1211	0.000	2.216	NO
6	GC-FID	0.1014	3.256	0.486	NO
8	GC-FID	0.0891	14.711	-0.591	NO
9	LC-UV	0.1000	20.000	0.368	NO
10	GC-MSD	0.1014	3.600	0.488	NO
14	GC-FID	0.0905	9.945	-0.464	NO
15	GC-FID	0.1100	0.000	1.244	NO
16	LC-UV	0.0740	5.405	-1.910	NO
17	GC-MSD	0.1012	7.217	0.469	NO
18	GC-FID	0.0863	5.449	-0.837	NO
19	LC-UV	0.0980	3.573	0.188	NO
20	GC-FID	0.1265	15.020	2.689	NO
21	GC-FID	0.1525	16.393	4.967	YES
22	LC-UV	0.0942	0.743	-0.145	NO
23	LC-UV	0.1271	0.866	2.737	NO
24	GC-FID	0.0842	0.989	-1.019	NO
27	GC-FID	0.1165	2.575	1.813	NO
29	GC-MSD	0.1960	0.000	8.777	YES
32	GC-FID	0.0895	7.821	-0.552	NO
35	GC-FID	0.1070	0.655	0.977	NO
36	GC-FID	0.1177	3.655	1.914	NO
37	LC-UV	0.1053	14.625	0.832	NO
38	GC-FID	0.0958	0.835	0.000	NO
39	LC-UV	0.1145	6.114	1.638	NO
40	GC-ECD	0.0950	6.316	-0.070	NO
41	GC-FID	0.0936	2.459	-0.197	NO
42	GC-FID	0.0970	0.000	0.105	NO
44	LC-MSD	0.0903	4.430	-0.482	NO
45	LC-UV	0.0965	1.036	0.061	NO
47	LC-UV	0.0940	2.128	-0.158	NO
50	GC-FID	0.0887	0.564	-0.626	NO
53	GC-FID	0.0850	11.765	-0.946	NO
54	GC-FID	0.0952	5.042	-0.053	NO
56	LC-UV	0.1739	0.805	6.841	YES
58 GC	GC-FID	0.0935	3.209	-0.201	NO
58 LC	LC-UV	0.1035	0.966	0.675	NO
59	GC-FID	0.0947	0.528	-0.101	NO
67	LC-MSD	0.1030	7.767	0.631	NO
68	LC-UV	0.0900	0.334	-0.512	NO
70	GC-FID	0.1380	4.348	3.697	YES
71	LC-UV	0.0893	0.000	-0.567	NO
73	GC-FID	0.0881	0.000	-0.675	NO
74	GC-FID	0.0872	2.294	-0.753	NO
76	LC-UV	0.0900	0.000	-0.508	NO
77	GC-FID	0.1980	5.051	8.952	YES
78	GC-FID	0.1105	15.385	1.288	NO
79	GC-FID	0.0867	0.808	-0.802	NO
80	GC-FID	0.1050	3.810	0.806	NO
81	GC-FID	0.0950	4.211	-0.070	NO
85	GC-FID	0.1050	9.524	0.806	NO
87	GC-FID	0.0863	2.667	-0.837	NO
88	GC-MSD	0.1700	11.765	6.500	YES
89	GC-FID	0.0835	0.719	-1.077	NO
90	LC-UV	0.0949	7.587	-0.079	NO
91	GC-FID	0.1048	1.336	0.788	NO
94	GC-FID	0.1100	0.000	1.244	NO
96	GC-FID	0.0897	2.566	-0.539	NO
97	GC-FID	0.0945	49.735	-0.114	NO
99	GC-FID	0.0870	0.000	-0.771	NO
100	GC-FID	0.0856	0.234	-0.893	NO
102	LC-MSD	0.0880	2.273	-0.683	NO
103	GC-FID	0.0985	1.015	0.237	NO
106	GC-FID	0.0900	0.334	-0.512	NO
107	LC-UV	0.1055	2.844	0.850	NO
109	LC-UV	0.1705	11.144	6.544	YES
110	GC-FID	0.0915	1.093	-0.377	NO

Lower Horwitz[3]	0.0774
Upper Horwitz[3]	0.1452
Grand Average[4]	0.105
Total SD[4]	0.026
Total Median[4]	0.096
MAD_E[5]	0.011

[1] Average yield and Relative Percent Difference between the two-day determinations per laboratory.
[2] An outlier is flagged when the modified Z-score falls outside the range of $-3.5 \leq Zi \leq 3.5$; see Appendix.
[3] Based on AAPCO adopted Allowed Deviations of Analytical Results from Label Claims, i.e. Horwitz limits for uniform samples based on median yield.
[4] Grand average, standard deviation, and median.
[5] Median Absolute Deviation Robust estimate of standard deviation; see Appendix for calculations.

AAPCO Check Sample 2016-1 is an opaque white herbicide with a claim of 41.5% 2,4-D, Acid Equivalent

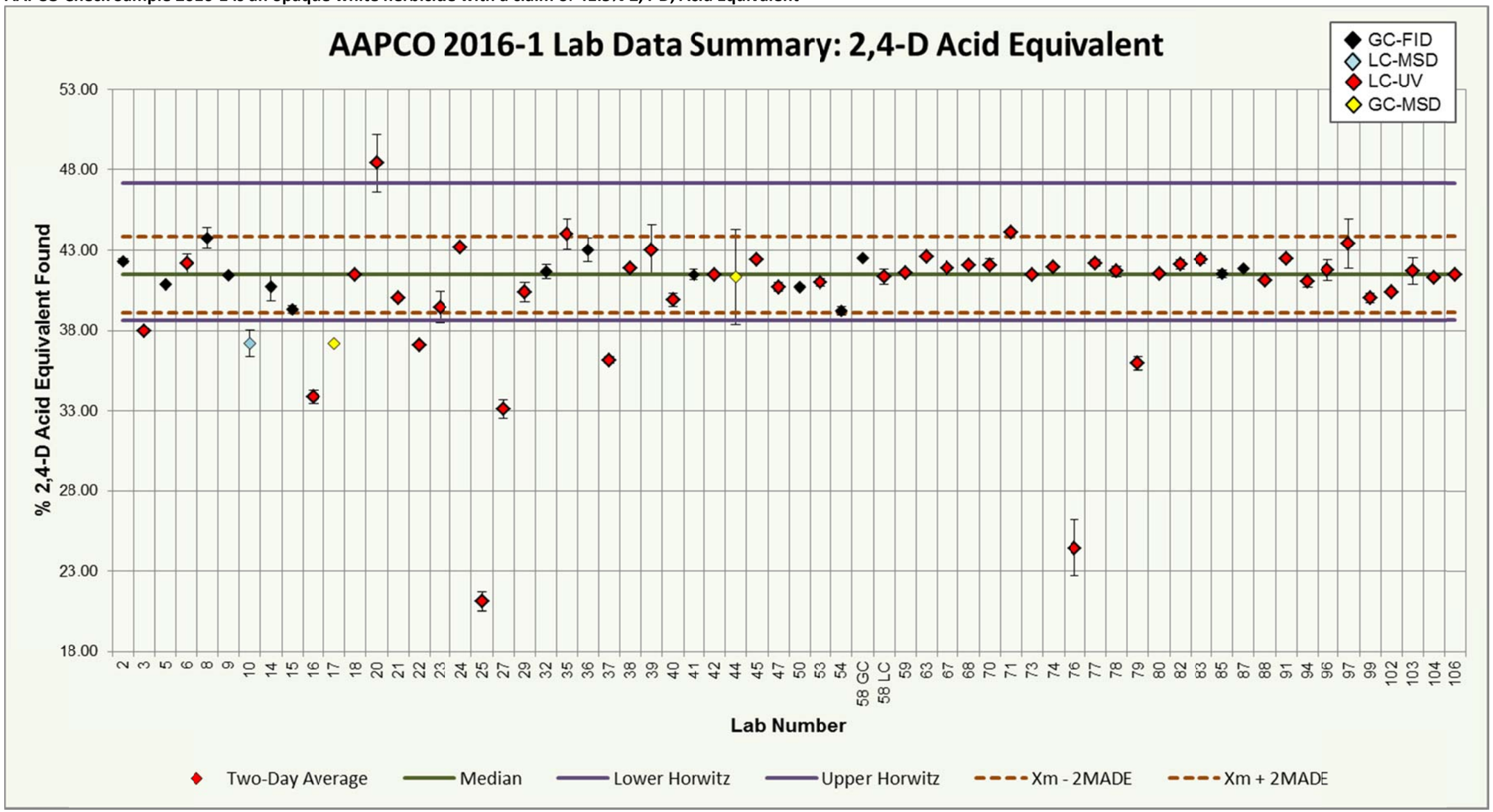

Figure 1a: Lab data summary of 2,4-D found in 2016-1. Mean assay result for each lab is shown with standard deviation from each lab depicted with vertical error bars. Marker color denotes chromatographic system used. Solid green line represents median of all data and dashed red lines represent the median ± 2 MAD_E. Purple solid lines indicate upper and lower Horwitz limits.

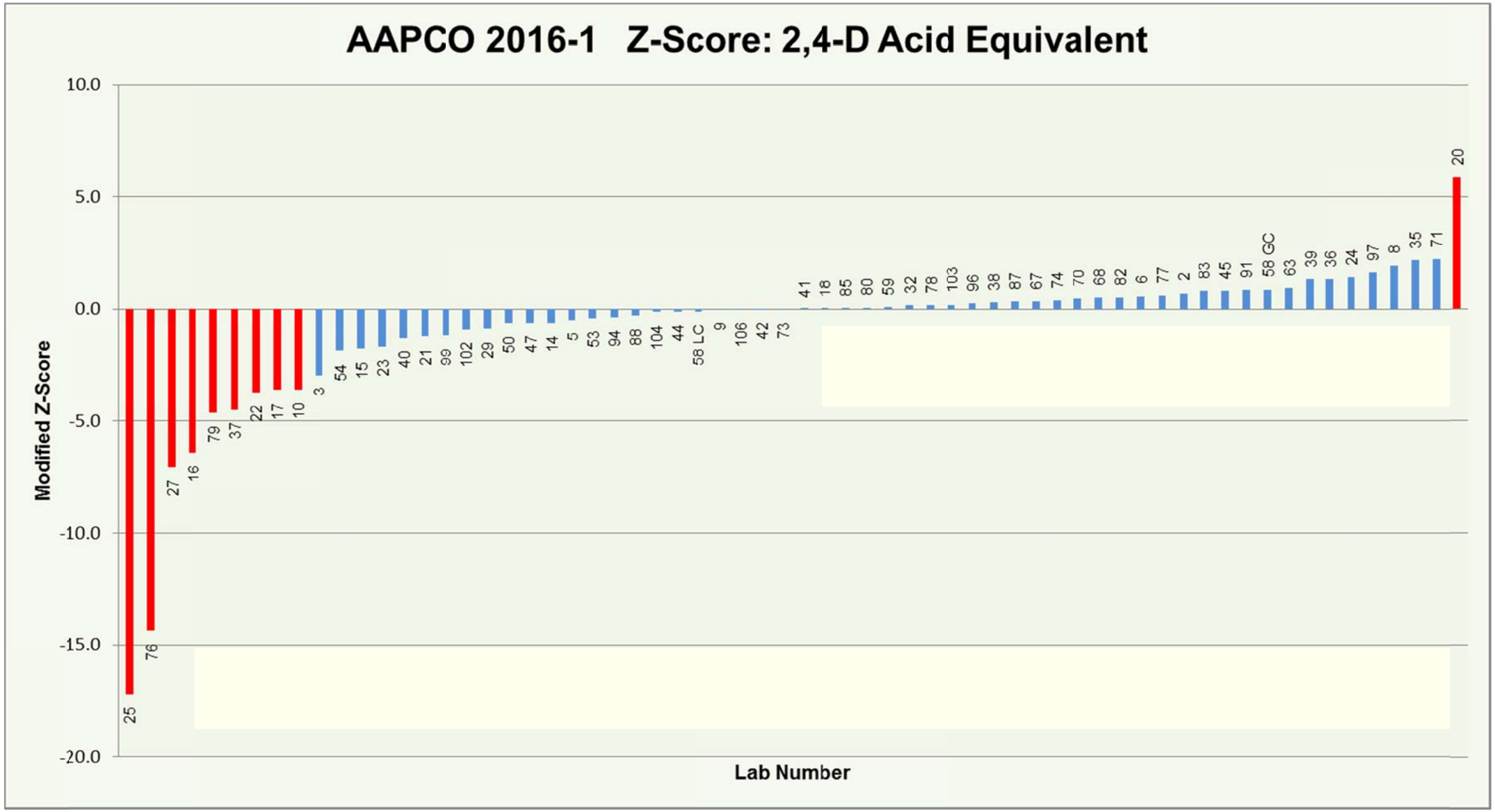

Figure 1b: Modified Z-score of each laboratory sorted from lowest to highest. Corresponding lab numbers are given next to the bars. Red bars indicate values that fall outside the acceptable Z-score range of -3.5 ≤ Zi ≤ 3.5. See Appendix for calculations.

AAPCO Check Sample 2016-1 is an opaque white herbicide with a claim of 62.6% 2,4-D, Isooctyl (2-ethylhexyl) ester form

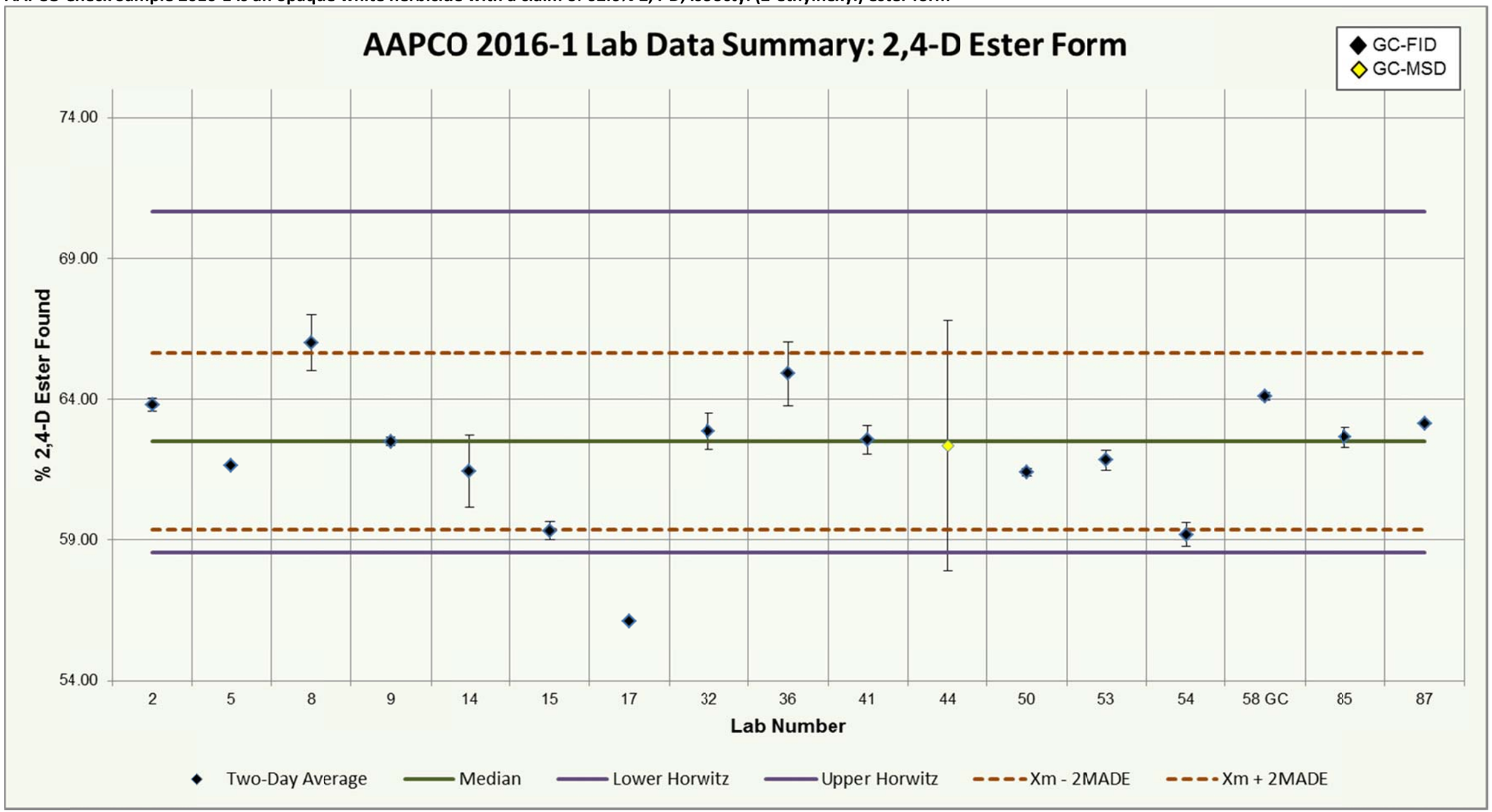

Figure 1c: Lab data summary of 2,4-D found in 2016-1. Mean assay result for each lab is shown with standard deviation from each lab depicted with vertical error bars. Marker color denotes chromatographic system used. Solid green line represents median of all data and dashed red lines represent the median ± 2 MAD_E. Purple solid lines indicate upper and lower Horwitz limits.

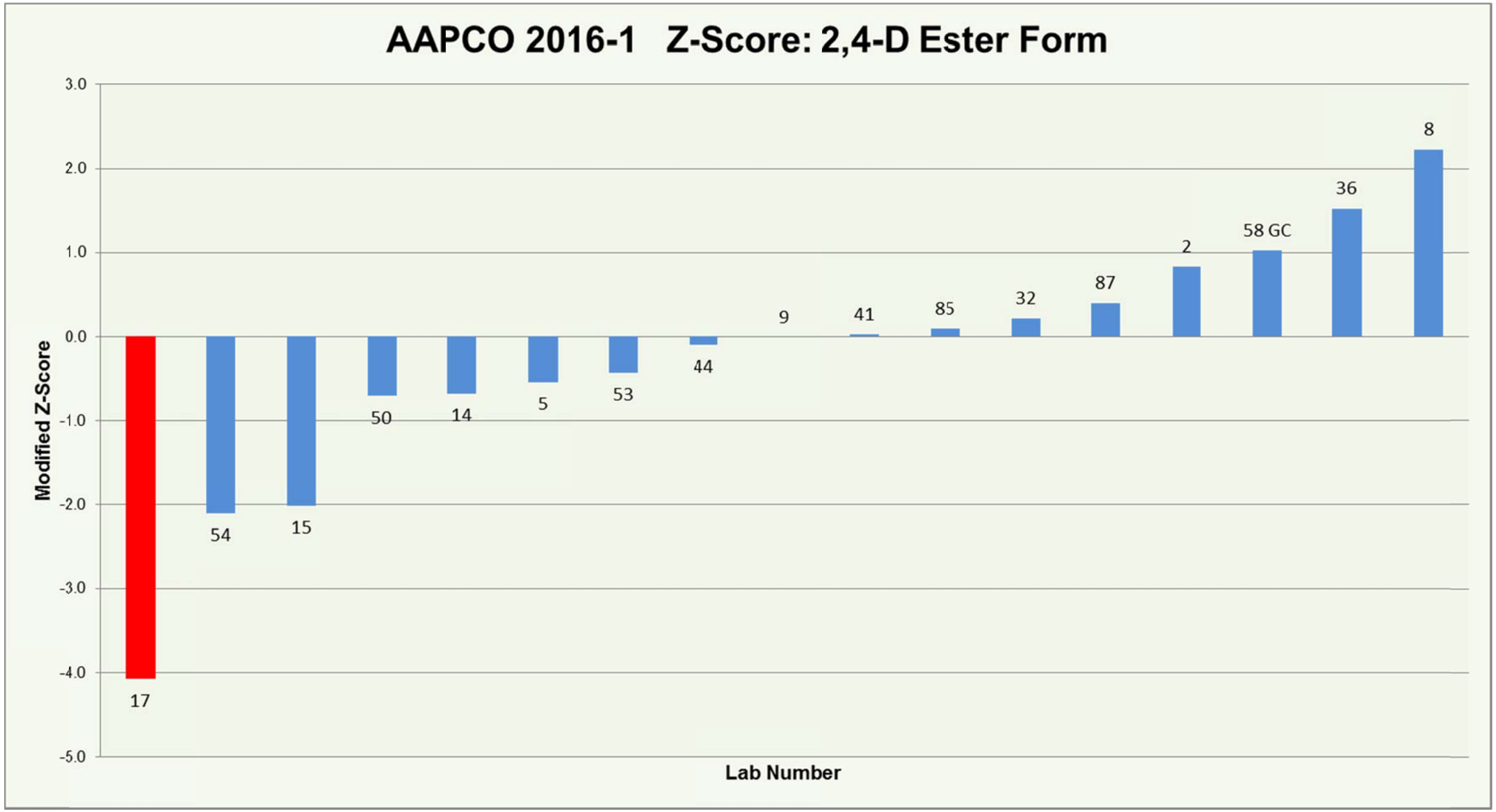

Figure 1d: Modified Z-score of each laboratory sorted from lowest to highest. Corresponding lab numbers are given next to the bars. Red bars indicate values that fall outside the acceptable Z-score range of -3.5 ≤ Zi ≤ 3.5. See Appendix for calculations.

AAPCO Check Sample 2016-2 is a transparent amber-colored herbicide with a claim of 41.0 Glyphosate IPA Salt (30.38% Glyphosate Acid Equivalent)

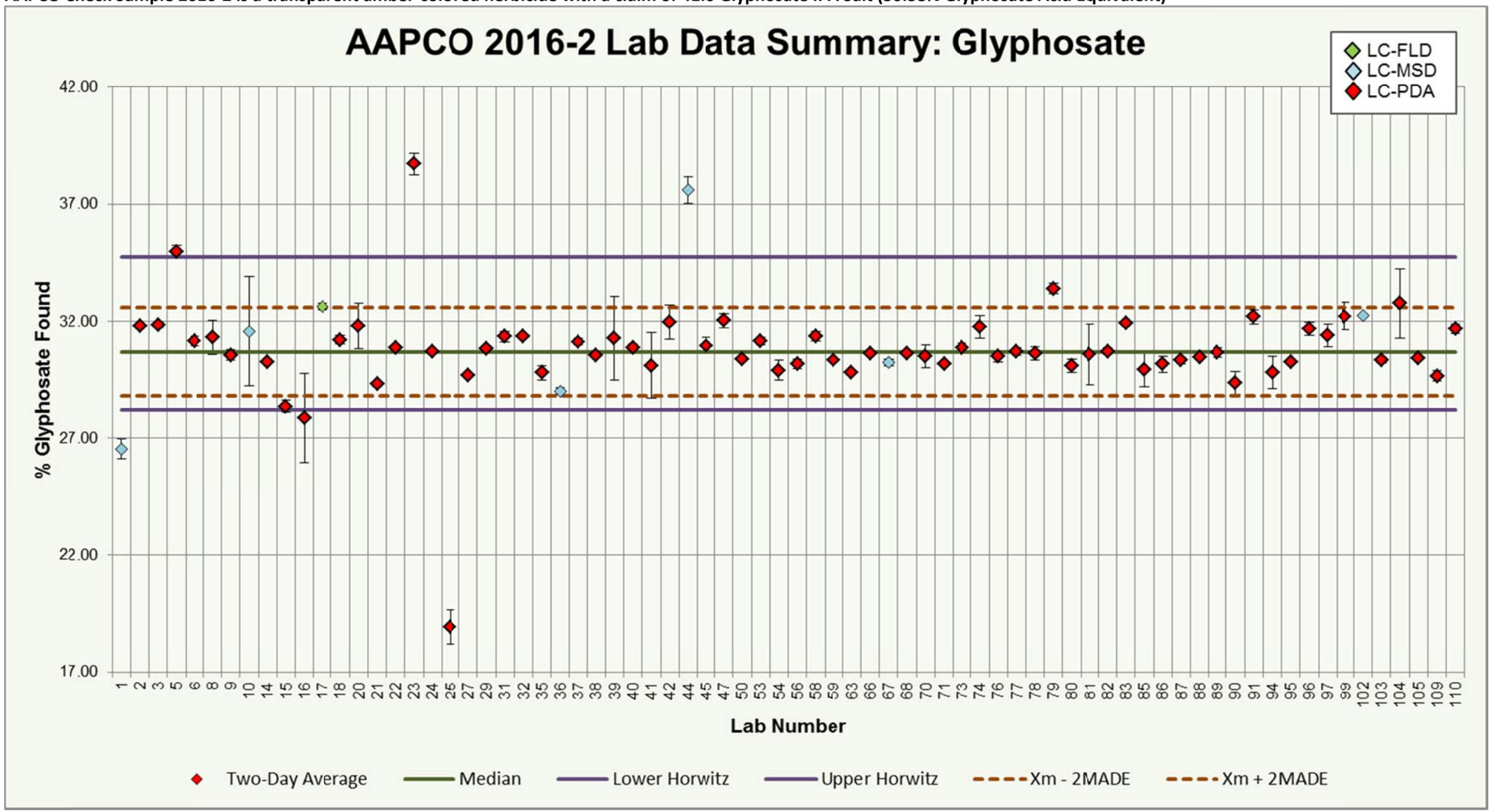

Figure 2a: Lab data summary of Glyphosate found in 2016-2. Mean assay result for each lab is shown with standard deviation from each lab depicted with vertical error bars. Marker color denotes chromatographic system used. Solid green line represents median of all data and dashed red lines represent the median ± 2 MAD_E. Purple solid lines indicate upper and lower Horwitz limits.

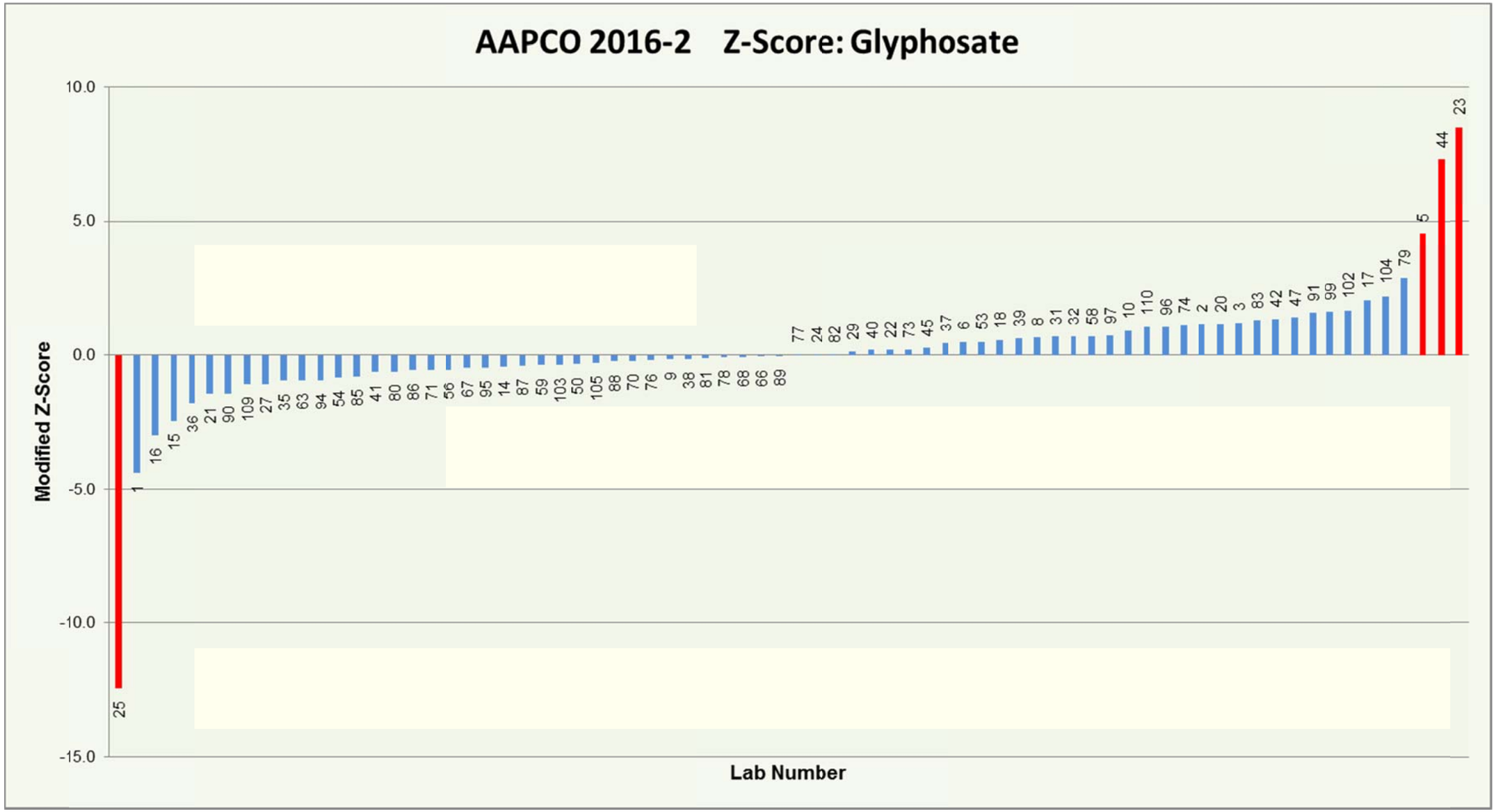

Figure 2b: Modified Z-score of each laboratory sorted from lowest to highest. Corresponding lab numbers are given next to the bars. Red bars indicate values that fall outside the acceptable Z-score range of -3.5 ≤ Zi ≤ 3.5. See Appendix for calculations.

AAPCO Check Sample 2016-3 is a granular insecticide with a claim of 0.5% Imidacloprid

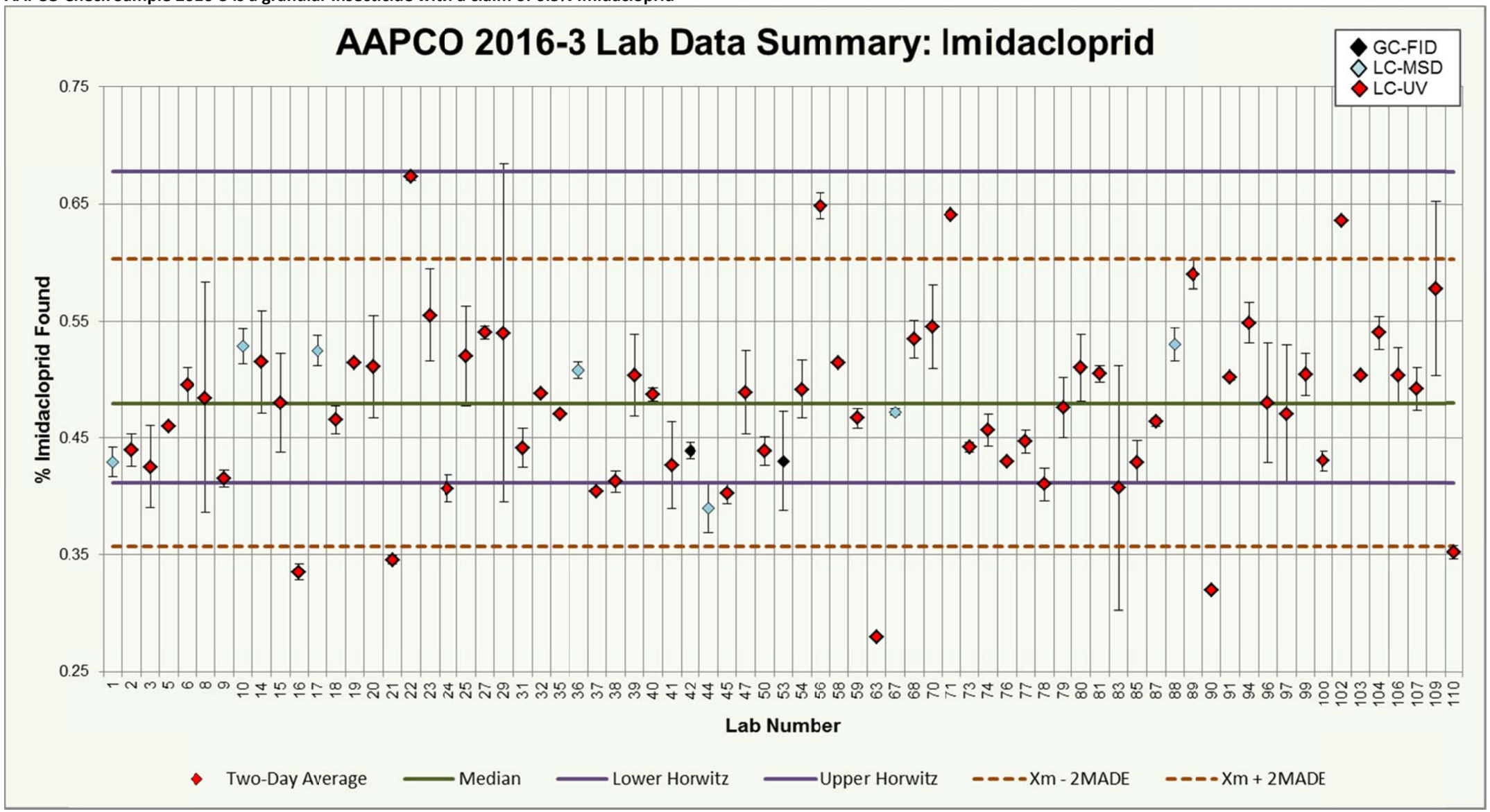

Figure 3a: Lab data summary of Imidacloprid found in 2016-3. Mean assay result for each lab is shown with standard deviation from each lab depicted with vertical error bars. Marker color denotes chromatographic system used. Solid green line represents median of all data and dashed red lines represent the median ± 2 MAD_E. Purple solid lines indicate upper and lower Horwitz limits.

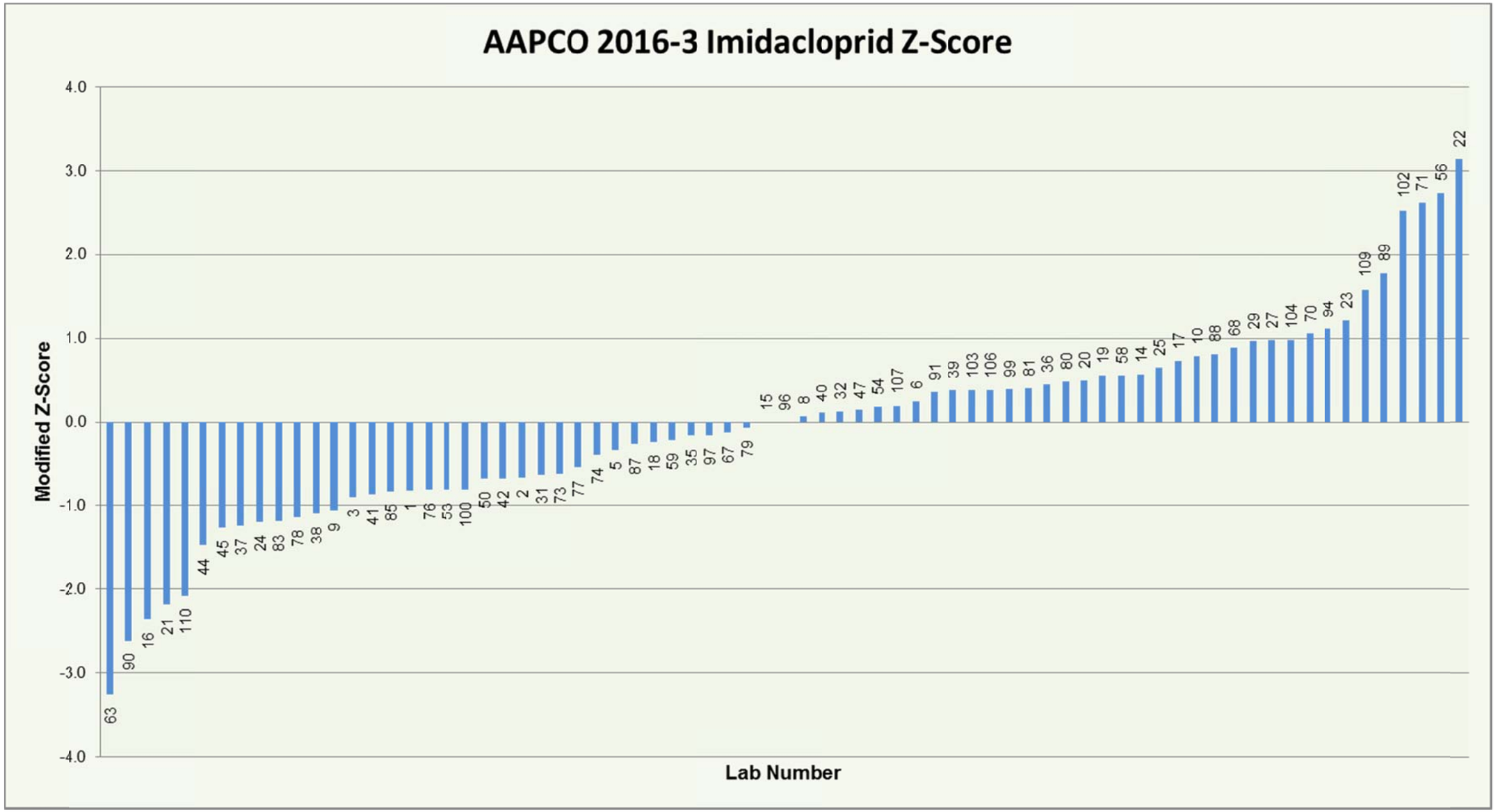

Figure 3b: Modified Z-score of each laboratory sorted from lowest to highest. Corresponding lab numbers are given next to the bars. Red bars indicate values that fall outside the acceptable Z-score range of -3.5 ≤ Zi ≤ 3.5. See Appendix for calculations.

AAPCO Check Sample 2016-3 is a granular insecticide with a claim of 0.1% Lambda-Cyhalothrin

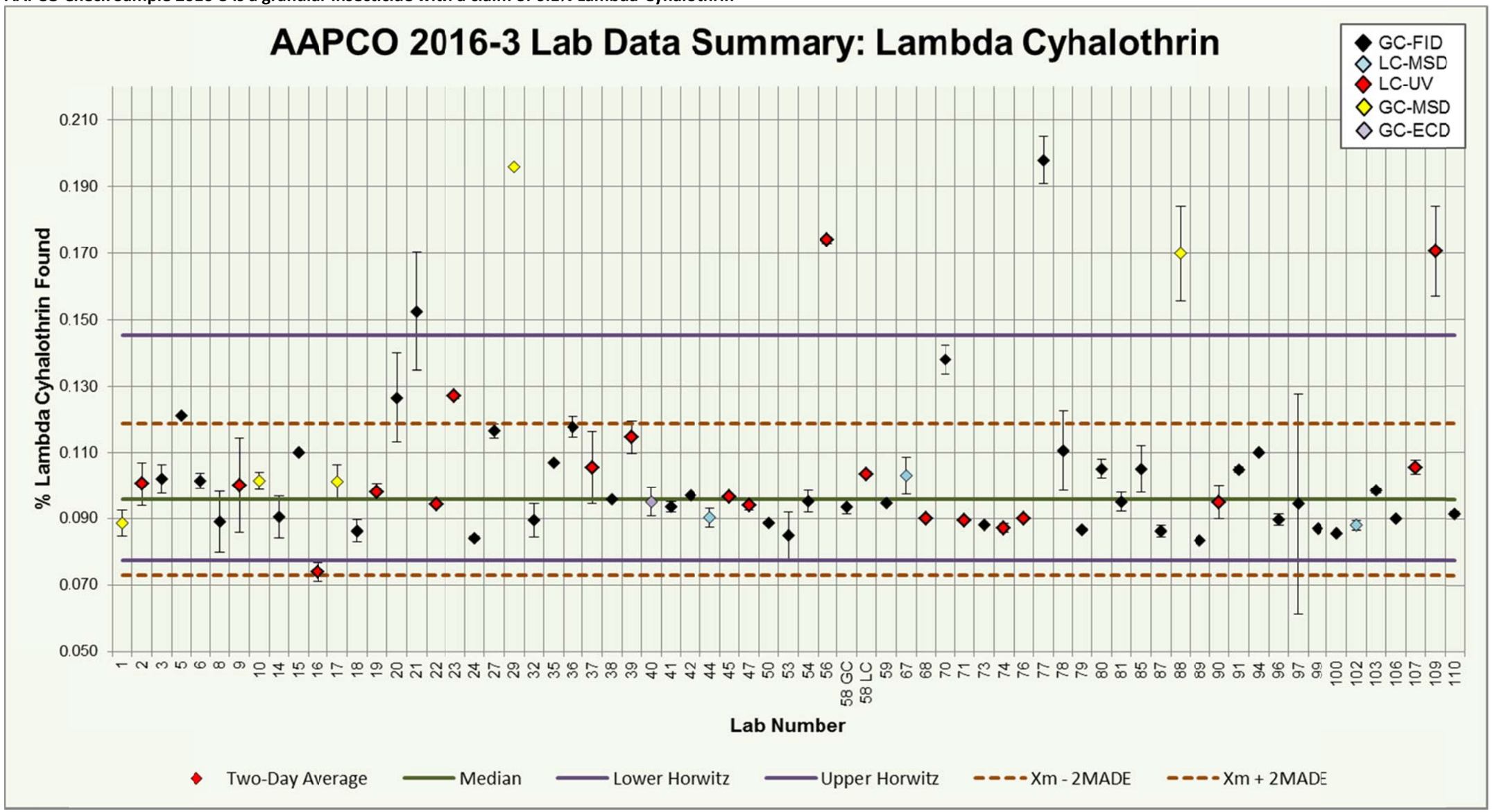

Figure 4a: Lab data summary of Lambda-Cyhalothrin found in 2016-3. Mean assay result for each lab is shown with standard deviation from each lab depicted with vertical error bars. Marker color denotes chromatographic system used. Solid green line represents median of all data and dashed red lines represent the median ± 2 MAD_E. Purple solid lines indicate upper and lower Horwitz limits.

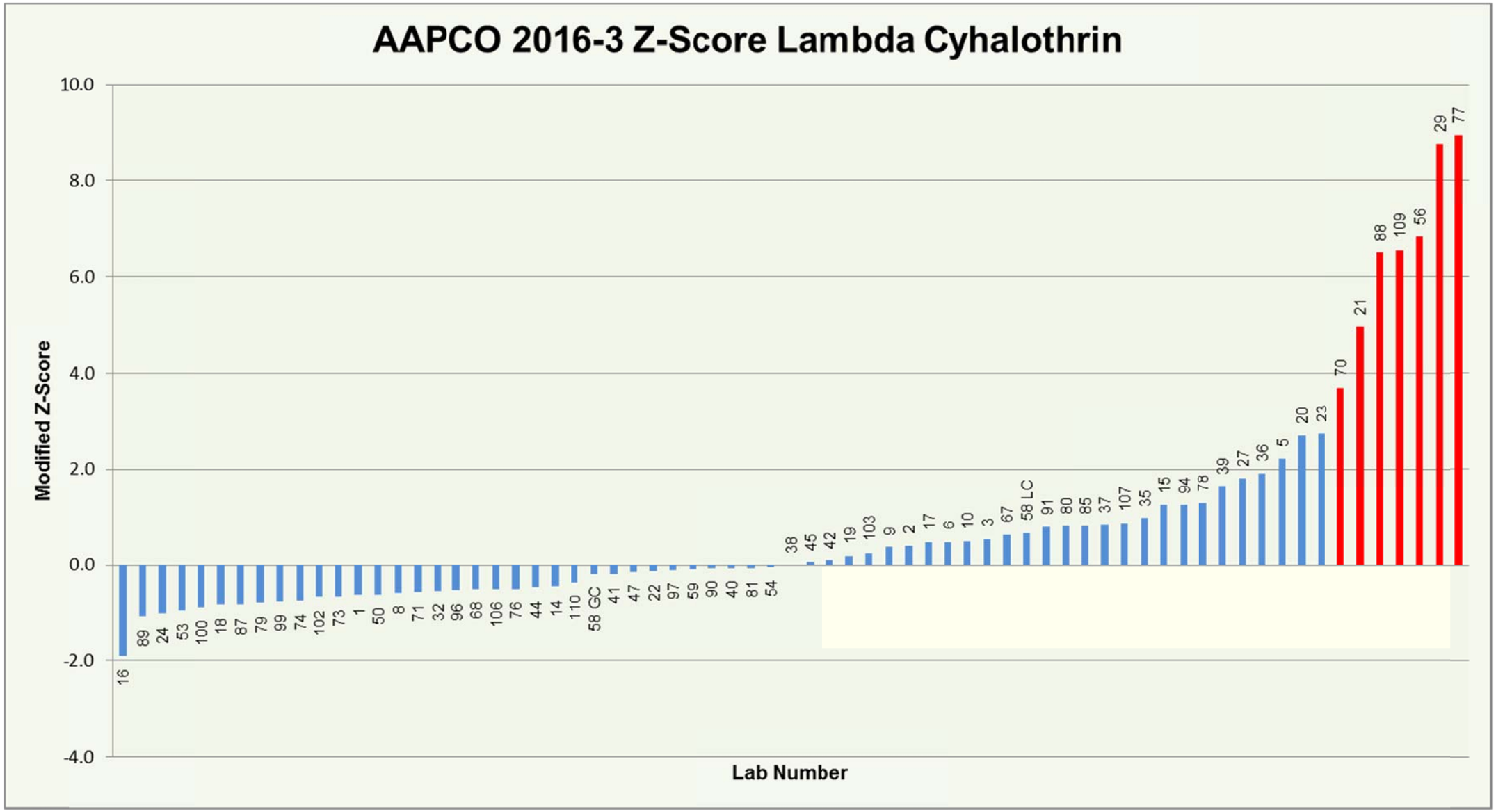

Figure 4b: Modified Z-score of each laboratory sorted from lowest to highest. Corresponding lab numbers are given next to the bars. Red bars indicate values that fall outside the acceptable Z-score range of -3.5 ≤ Zi ≤ 3.5. See Appendix for calculations.

Table 7: Representative LC Methods for the determination of 2,4-D

Lab #	Reference Methods	Internal Standard	Extractants	Sample Preparation	Mobile Phase	Detector	Wavelength (nm) or MRM Transition (m/z)	Column
6, 23, 29, 35, 40, 42, 58, 59, 73, 74, 76, 77, 102, 103, 104 10	• OPPTS Guideline 830.1800 • In-House • Manufacturer Method	• None • 1-Methyl-2-pyrrolidone • 2,4,5-T	4-5% Potassium Hydroxide in Water 95-96% Methanol	• Add extraction solvent • 10-30 minute sonication • 12 hour/overnight saponification • Filter	A: 0 to 9.3% Acetic Acid in Water B: 0 to 9% Acetic Acid in Methanol (or Acetonitrile) A: 5mM Formic Acid in Water B: 5mM Formic Acid in Acetonitrile	UV MSD	280 254 275 219.0 > 160.9 219.0 > 125.0	Zorbax Eclipse XBD-C18 (5µ, 4.6x150mm) Partisil 10 ODS-2 (5µ, 4.6x250mm) Thermo Acclaim C18 (5µ, 4.6x150mm) Zorbax SB C18 (5µ, 4.6x250mm) Hypersil ODS (5µ, 4.0x125mm) Poroshell 120 EC-C18 (2.7µ, 4.6x50mm) Spherisorb Amino NH2 (3µ, 4.6x150mm) Restek Ultra AQ C18 (5µ, 4.6x150mm) SphereClone ODS(2) (5µ, 4.6x250mm) Kinetex EVO (5µ, 4.6x250mm) YMC-Pack Pro C18 (3µ, 4.0x150mm) Eclipse Plus C18 (3.5µ, 4.6x100mm) Eclipse C18 (1.8µ, 2.1x50mm) Poroshell 120 EX-C18 (2.7µ, 2.1x100mm)
16, 68, 106	• CIPAC 1C*1/TC/M3 • In-House	• 4-bromophenol • None	67% 0.2M Potassium Hydroxide in Isopropanol 33% Water	• Add extraction solvent • 10-15 minute sonication • Allow to cool to room temp • Filter	A: 60% Phosphate Buffer (or Water) B: 40% Acetonitrile	UV	280	Zorbax Eclipse XBD-C18 (5µ, 4.6x150mm) ODS C18 (5µ, 4.6x250mm)
16, 21, 27, 63, 71, 96	• In House	• None	Acetonitrile	• 20 min sonication • Filter	A: 6mM Potassium Phosphate (pH 2.5) (or Water) B: Acetonitrile	UV	280 235/240 230	Bondclone C18 (10µ, 3.9x150mm) Alltima Phenyl (3µ, 4.6x100mm) Luna (5µ, 4.6x150mm) Intersil ODS-3 (5µ, 4.6x250mm) Chromanik C-18 (5µ, 4.6x250mm) Kinetex C18 (2.6µ, 4.6x100mm)
20, 45	• AOAC 978.05 • In-House	• None	65% Isopropanol 35% 0.2M Potassium Hydroxide in Water	• Heat 15 min in 50°C • Shake 1 hour • Filter	4:15:1 Acetonitrile: Water: 6N NaOH (pH 2.95)	UV	280	Partisil 10-SAX (10µ, 4.6x150mm) Gemini C18 (10µ, 4.6x250mm)
22, 78	• In-House	• None	Methanol	• Vortex 30 seconds • 15 minute saponification • Dilute to volume	A: 95% Methanol B: 5% Acidified Water (0.05 or 1% Phosphoric Acid)	UV	235 230	Supelco Discovery C18 (5µ, 4.6x250mm) LiChrospher 100 RP18 (5µ, 4.0x250mm)
24, 38, 39, 94	• In-House	• None	65% (or 50%) Isopropanol 35% (or 50%) 0.2M Potassium Hydroxide in Water	• Heat 40 min in 60°C o 1 hour at 190°C o 30 min at 70°C • Sonicate 15-30 minutes o 2 hours at 100°C o No sonication • Cool and filter	A: Acidified Water B: Acidified Methanol	UV	280	Phenomenex ODS (5µ, 4.6x250mm) XTerra RP18 (5µ, 4.6x150mm) Eclipse XDB-C8 (5µ, 4.6x150mm) LiChrospher RP-18 (5µ, 4.0x250mm)

Table 7 (continued): Representative LC Methods for the determination of 2,4-D

Lab #	Reference Methods	Internal Standard	Extractants	Sample Preparation	Mobile Phase	Detector	Wavelength (nm) or MRM Transition (m/z)	Column
47	• AOAC 984.07 and Manufacturer method	• None	0.125M Sodium Hydroxide in Methanol	• Overnight saponification • Neutralize with 9.5% Acetic Acid • Dilute to volume with Methanol	A: Phosphate Buffer (pH 2.7) B: Acetonitrile	UV	280	Kinetex Biphenyl (5µ, 4.6x150mm)
67	• AOAC 978.05	• None	0.1N Potassium Hydroxide in Methanol	• Add extraction solvent • Heat 20 min in 50°C • Sonicate at 50°C for 15 min	A: Acidified Water B: Acidified Acetonitrile	UV	281	XBridge C18 (3.5µ, 2.1x50mm)
80, 82	• In-House	• None	Potassium Hydroxide in Methanol/Water	• Sonicate for 15 min	A: 0.5 M NaOH (pH 2.95) or 0.1% Phosphoric Acid B: Acetonitrile	UV	270 283	Eclipse XBD C8 (5µ, 4.6x150mm) Hypersil ODS (5µ, 4.6x250mm)
70, 83, 99	• Manufacturer Method • In-House • CIPAC 1C	• Triphenyl Phosphate • None	Saponification Solution (or Water) and Acetonitrile	• Add saponification solution • 15 minute sonication • Dilute to volume with Acetonitrile	A: Water B: Acidified Methanol (or Acidified Acetonitrile)	UV	280 220	Waters HSS T3 (1.8µ, 2.1x100mm) Shimpack CLC-ODS(M) (5µ, 4.6x250mm) LiChrospher RP-18

Table 8: Representative GC Methods for the determination of 2,4-D

Lab Number	Reference Methods	Internal Standard	Extractants	Sample Preparation	Injector Type and Temperature	Oven Temperature	Detector	Column
8. 14, 15, 17, 32, 36, 41, 50, 54, 85	In-House	• None • DIbutyl phthalate	Acetone	• Dilute • 3-30 minute sonication	*Splitless:* 225-300°C *Split:* Ratio: 20:1 to 30:1 Temp: 250-270°C	*Gradient:* Initial Temp:70-190°C Final Temp: 250-300°C *Isothermal:* 230°C	FID MSD	ZB-1 (30m x 0.32mm x 1µm) RTX-5 (15m x 0.53mm x 1.5µm) VF-5MS (30m x 0.25mm x 0.25µm) DB-5 (30m x 0.53mm x 1.5µm) RTX-5Sil MS (30m x 0.25mm x 0.25µm) RTX-CLPesticides2 (30m x 0.53mm x 0.42µm) CPSil13CB (25m x 0.32mm x 0.2µm) DB-5MS (30m x 0.25mm x 0.25µm) HP-5 (30m x 0.32mm x 0.25µm)
2	In-House	• None	Chloroform	• Dilute • 10 minute sonication	*Splitless:* 230°C	*Isothermal:* 220°C	FID	DC200 (1.2ft x 2mm)
44	In-House	• None	Methyl tert-butyl ether	• Dilute • 20 minute sonication	*Splitless:* 250°C	*Gradient:* Initial Temp: 100°C Final Temp: 320°C	MSD	ZB-5MS Guardian (20m x 0.18mm x 0.18µm)
5, 9	In-House	• None	Acetonitrile	• Dilute • 30 minute sonication o Or none	*Split:* Ratio: 5:1 to 20:1 Temp: 180-230°C	*Gradient:* Initial Temp: 80-180°C Final Temp: 270-320°C	FID	Rxi-1MS (30mx x0.32mm x 0.25µm) DB-5 (30m x 0.32mm x 1.5µm)
58	In-House	• DIbutyl phthalate	Methanol	Dilute and shoot	*Split:* Ratio: 50:1 Temp: 300°C	*Gradient:* Initial Temp: 210°C Final Temp: 270°C	FID	HP-5 (30m x 0.32mm x 0.25µm)
87	In-House	• DIbutyl phthalate	Methyl isobutyl ketone	Sonicate	*Split:* Ratio: 60:1 Temp: 250°C	*Isothermal:* 210°C	FID	Supelco MDN-12 (30m x 0.25mm x 0.25µm)

Table 9: Representative LC Methods for the determination of Glyphosate

Lab #	Reference Methods	Extractants	Sample Preparation	Mobile Phase	Detector	Wavelength (nm) or MRM Transition (m/z)	Column
1, 67	• In-House	Water	• Dilute and shoot	A: 20mM Ammonium Formate (pH 3) or 0.1% Formic Acid B: Acetonitrile	MSD	168.02 > 149.5 171.02 > 152.5	Kinetex Hilic (2.6µ, 2.1x50mm) Sielc Obilisc N (5µ, 2.1x150mm)
10, 44	• In-House	Water	• Dilute • Derivatize with FMOC	A: 10mM Ammonium Acetate B: Acetonitrile	MSD	390.0 > 168.0 390.0 > 150.0 391.8 > 179.0 391.8 > 87.9	Hypersil Gold (5µ, 2.1x150mm) Acquity HSS T3 (1.7µ, 2.1x100mm)
35	• In-House	Water + 5% Acetonitrile + 5mM Ammonium Acetate	• Dilute • Sonicate	A: Water + 5% Acetonitrile + 5mM Ammonium Acetate B: Acetonitrile	MSD	167.9 > 150 (-)	Acquity BEH C18 (1.7µ, 2.1x150mm)
102	• In-House	Water	• Dilute • 10-30 minute sonication	A: Water B: 1mM Citric Acid in Water (pH 9.5)	MSD	168.2 > 62.8 168.2 > 79	Dionex Ionpac AS11 (2x250mm)
2, 3, 6, 16, 18, 20, 21, 22, 24, 25, 27, 37, 40, 59, 66, 73, 79, 81, 96, 103, 104	• CIPAC 284 • In-House • AOAC 983.10 • Gavlick & Tomkins 2008	70-100% Water 0-30% Methanol	• Dilute • Shake 3-45 minutes o 30 second vortex • 3-30 minute sonication o 45 min sonic/vortex • Cool and Filter • Or Dilute and Shoot	A: Phosphate Buffer (pH 1.9-2.68) B: Methanol	UV	190 195 198 200 205 254	Waters SAX (5µ, 4.6x250mm) Dionex Ionpac AS11 (2x250mm) Partisil SAX (10µ, 4.6x250mm) (5µ, 4.6x100mm) Zorbax SAX (5µ, 4.6x150mm) (5µ, 4.6x250mm) Adsorbosphere SAX XL (4.6x250mm) Grace Platinum SAX (3µ, 7x53mm) Whatman MAX-1 (5µ, 4.6x250mm) Hamilton PRP-X 100 (10µ, 4.1x150mm) Acquity BEH Amide (1.7µ, 2.1x100mm)
14, 15, 29, 35, 38, 41, 45, 50, 54, 56, 58, 63, 68, 70, 74, 76, 77, 78, 80, 82, 83, 84, 85, 86, 87, 88, 89, 94, 95, 97, 105, 110	• CIPAC 284 • In-House	88-96% Phosphate buffer (pH 1.9-2.3) 4-12% Methanol	• Dilute • 5-20 minute sonication o Shake 15 minutes • Filter	A: 88-96%Phosphate Buffer B: 4-12% Methanol	UV	190 195 196 200	Phenosphere SAX 80A (5µ, 4.6x250mm) Zorbax SAX (5µ, 4.6x250mm) (5µ, 4.6x150mm) Sphereclone SAX (5µ, 4.6x250mm) Zorbax NH2 (5µ, 4.6x150mm) Phenomenex NH2 80A (5µ, 4.6x150mm) Whatman MAX 1 WCS (5µ, 4.6x250mm) Nucleosil 100-5 SB (5µ, 2.6x250) YMC-Pack Pro C18 (3µ, 4.0x150mm) Hamilton PRP-X 100 (10µ, 4.1x150mm) Interchim Uptisphere SAX (5µ, 4.6x250mm)
17	• Pickering Post-column Derivatization	0.1% Formic Acid in Water	• Dilute • Shake and let stand	A: Pickering K200 B: Pickering RG019	UV	Ex @ 330 Em @ 466	Pickering Glyphosate K+ (8µ, 4.0x150mm)
39	• In-House	Acidified Water	• Dilute with Acidified Water • Add Potassium Bromide + Sodium Nitrite • Derivatize 45 minutes	3% Acetic Acid in Water	UV	244	Eclipse XBD-C8 (5µ, 4.6x150mm)

Table 10: Representative LC Methods for the determination of Imidacloprid

Lab #	Reference Methods	Internal Standard	Extractants	Sample Preparation	Mobile Phase	Detector	Wavelength (nm) or MRM Transition (m/z)	Column
1, 10, 17, 36, 44, 88	• In-House	• Clothianidin • None	Acetonitrile (or Methanol)	• Dilute • 10-30 minute sonication o Let sit 2 hours • Dilute with water (or mobile phase A) for 10% organic	A: 10:90 Water:Methanol + 0.1-1% Formic Acid (or 5mM Formic Acid) (or 0.1% Acetic Acid) B: 90:10 Water:Methanol + 0.1-1% Formic Acid (or 5mM Formic Acid) (or 0.1% Acetic Acid)	MSD	256.7 > 176.1 257.7 > 120.1 257.7 > 176.1 256.158 > 209.08 256 > 209 255.9 > 209.1 255.9 > 175.08 256 > 175 256 > 209	Kinetex C18 (2.6µ, 2.1x50mm) Poroshell 120 EC-C18 (2.7µ, 2.1x100m) Zorbax SB-C18 (3.5µ, 2.1x150mm) Acquity BEH C18 (1.7µ, 2.1x150mm) Acquity BEH C18 (1.7µ, 2.1x50mm) LaChrom Purosphere Star RP-18 (3µ, 4.0x125mm)
2, 3, 5, 8, 9, 14, 16, 20, 27, 29, 35, 38, 41, 50, 56, 70, 71, 74, 76, 77, 78, 79, 80, 81, 83, 87, 89, 90, 94, 96, 97, 99, 100, 102, 103, 104, 107, 109, 110	• CIPAC 582 • In-House • CA Dept of Ag • AOAC 997.12 • Manufacturer method	• None • Propiophenone • 4'-Nitroacetophenone	Acetonitrile (or 10-50% Water)	o Grind sample • Dilute • 3-60 minute shake • 10-15 minute sonication o Allow to sit overnight o Dilute with water for 30-60% organic • Centrifuge • Filter	A: 20-50% Water (or 0.1M Sodium Citrate + 0.1M HCl) (or 0.1% Phosphoric Acid) (or 2% Acetic Acid) B: 50-80% Acetonitrile	UV	215 235 240 252 254 260 265 269 269.4 270 272 278 280	Nucleosil C18 (5µ, 4.6x250mm) Zorbax XDB-C18 (3.5µ, 4.6x150mm) ACE 5 C18 (5µ, 4.6x250mm) Zorbax SB-C18 (5µ4.6x250mm) Poroshell 120 EC-C18 (2.7µ, 4.6x50mm) Eclipse XBD C18 (5µ, 4.6x150mm) Ultra C18 (5µ, 4.6x250mm) Kinetex EVO C18 (5µ, 4.6x150mm) Agilent SB Phenyl (5µ, 4.6x150mm) Synergi Max-RP (4µ, 4.6x150mm) Hypersil ODS (5µ, 4.0x125mm) Sunfire C18 (5µ, 4.6x150mm) Xterra RP18 (5µ, 4.6x150mm) Discovery HS-C18 (5µ, 4.6x150m) Synergi Fusion HydroRP (4µ, 4.6x250mm) Alltima Cyano (5µ, 4.6x250mm)
15, 22, 23, 25, 31, 39, 45, 58, 63, 68, 73, 85, 91,	• In-House • Manufacturer method	None	Methanol (or 50% Water) (or Acidified Water)	• Dilute • 20-60 minute sonication o 30 second vortex • Cool	A: Water (or 0.05-1% Phosphoric Acid) (or 0.5-3% Acetic Acid) B: Methanol	UV	212 235 252 265 269 270 310	Partisil 10 ODS3 (5µ, 4.6x150mm) Discovery C18 (5µ, 4.6x250mm) Partisphere RTF C18 (5µ, 4.6x250) LiChrosorb RP-18 (5µ, 4.6x200mm) Eclipse SDB-C8 (5µ, 4.6x150mm) Gemini C18 (10µ, 4.6x250mm) Zorbax SB-C18 (5µ, 4.6x250mm)
18	• In-House Normal Phase	Acetophenone	50:50 Isopropanol: Heptane	• 20 minute sonication • 1 hour shaker	A: Hexane B: 62.5:37.5 IPA:Heptane	UV	252	Eclipse XDB-CN (3.5µ, 4.6x150mm)

Table 10 (continued): Representative LC Methods for the determination of Imidacloprid

Lab #	Reference Methods	Internal Standard	Extractants	Sample Preparation	Mobile Phase	Detector	Wavelength (nm) or MRM Transition (m/z)	Column
24	• In-House	None	Isopropanol	• Add IPA • Grind for 20 minutes @ 1600 rpm • 1 hour sonication, then cool • Dry aliquot with N2 to dryness • Add IPA and vortex 10 sec. • Filter	A: 0.1% Formic Acid + 10mM Ammonium Formate in Water B: 0.1% Formic Acid + 10mM Ammonium Formate in Methanol	UV	270	Prodigy ODS(3) 100A (5µ, 4.6x250mm)
37	• In-House	None	Acetone	• Add Acetone • Stir 1 hour • Filter	A: 60 to 10% Water (gradient) B: 40 to 90% Acetonitrile (gradient)	UV	225	Zorbax SB-C18 (5µ, 4.6x150)
6, 40, 59	• Manufacturer method	• 4'-Nitroacetophenone • None • Propiophenone	Methylene Chloride	• Add MeCl2 • 5-15 minute sonication • 30-60 minute shake • Filter/centrifuge	A: 40% Water B: 60% Acetonitrile	UV	252	XBridge C18 (5µ, 4.6x150mm) Zorbac ODS (5µ, 4.6x250mm) SphereClone ODS (2) (5µ, 4.6x250mm)
67	• In-House	• None	Acetone/Acetonitrile	• Dissolve in Acetone • Boil gently 5 minutes • 30 minute sonication • Dilute with Acetonitrile	A: 5mM Ammonium Acetate in 10% Methanol B: 5mM Ammonium Acetate in 90% Methanol	MSD	256 > 208 256 > 175.2	Acquity HSS T3 (1.8µ, 1x100mm)

Table 11: Representative GC Methods for the determination of Imidacloprid

Lab Number	Reference Methods	Internal Standard	Extractants	Sample Preparation	Injector Type and Temperature	Oven Temperature	Detector	Column
42, 53	In-House	• None • Dicyclohexyl phthalate	• Acetone + Ethyl Acetate • Acetone + Trifluroacetic Acid	• Dilute • 20-30 minute sonication	*Splitless:* 220°C *Split:* Ratio: 25:1 Temp: 300°C	*Gradient:* Initial Temp:160-250°C Final Temp: 280-300°C	FID	DB-17 (30m x 0.25mm x 0.25µm) RTX-5W (30m x 0.53mm x 0.5µm)

Table 12: Representative GC Methods for the determination of Lambda-Cyhalothrin

Lab Number	Reference Methods	Internal Standard	Extractants	Sample Preparation	Injector Type and Temperature	Oven Temperature	Detector	Column
1, 17, 29	In-House	• 2,4,6-Tribromobiphenyl • None	• Acetone	• Dilute • 30 minute sonication • 30 minute shake • Filter	*Splitless:* 240-280°C *Split:* Ratio: 25:1 Temp: 300°C	*Gradient:* Initial Temp:50-100°C Final Temp: 280-320°C	MSD	ZB-MR-1 (30m x 0.25mm x 0.25µm) VF-5MS (30m x 0.25mm x 0.25µm)
5, 10, 35, 44, 78, 79	In-House	• None • Bis 2-(ethylhexyl Phthalate)	• Acetonitrile • MeCN + 0.04% Trifluoroacetic Acid	• Dilute • 5-30 minute sonication • 30 minute shake • Filter	*Splitless: 140*-250°C *Split:* Ratio: 5:1 to 20:1 Temp: 230-300°C *2 minute Gradient:*45°C to 280°C	*Gradient:* Initial Temp: 8-180°C Final Temp: 280-320°C *Isothermal:* 240°C	MSD FID	Rxi-5Sil MS (30m x 0.25mm x 0.25µm) HP-5 (30m x 0.32mm x 0.25µm) ZB-5MS (20m x 0.18mm x 0.18µm) Rxi-1MS (30m x 0.32mm x 0.25µm) ZB-5 (30m x 0.32mm x 0.25µm) VF-5MS (30m x 0.25mm x 0.25µm)
3, 8, 14, 15, 20, 21, 32, 36, 38, 41, 42, 50, 59, 70, 73, 74, 77, 80, 81, 85, 87, 89, 91, 94, 96, 100	• In-House • AOAC 998.01 • CIPAC 463 • Manufacturer method	• None • Dicyclohexyl Phthalate • Diethyl Phthalate • Dioctyl Phthalate	• Acetone • Acetone/Ethyl Acetate • Ethyl Acetate	• Dilute • 3 minute-4 hour shake • 5-60 minute sonication • Cool • Filter	*Splitless:* 200-250°C *Split:* Ratio: 2:1 to 150:1 Temp: 180-300°C	*Gradient:* Initial Temp: 65-240°C Final Temp: 250-300°C *Isothermal:* 230-280°C	FID	DB-5 (30m x 0.32mm x 0.25µm) (0.53mm x 1.5µm) DB-5MS (30m x 0.32mm x 0.25µm) ZB-1 (30m x 0.32mm x 1µm) RTX-5 (15m x 0.53mm x 1.5µm) (0.25mm x 0.25µm) DB-35 (30m x 0.32mm x 0.25µm) DB-17 (30m x 0.53mm x 0.5µm) RTX-5Sil MS (30m x 0.25mm x 0.25µm) RTX-CLPesticides2 (30m x 0.53mm x 0.42µm) RTX-5W (30m x 0.53mm x 0.5µm) HP-1 (30m x 0.53mm x 1.5µm)
97, 99, 103, 106, 110	• In-House • CIPAC 463	• Dioctyl Phthalate • None • Bis 2-(ethylhexyl Phthalate)	• Dichloromethane • Acetone/MeCl2 • Chloroform	• Dilute • 3 minute shake • 15 minute sonication • Filter	*Splitless:* 300°C *Split:* Ratio: 10:1 to 60:1 Temp: 280-300°C	*Isothermal:* 230-240°C	FID	DB-1701 (15m x 0.53mm x 1µm) HP-5 (30m x 0.32mm x 0.25µm) DB-1 (30m x 0.25mm x 0.25µm)
18	Manufacturer method	• Dicyclohexyl Phthalate	• Toluene	• Dilute • 1 hour shake • Filter	*Splitless:* 250°C	*Gradient:* Initial Temp: 220°C Final Temp: 250°C	FID	HP-50+ (30m x 0.536mm x 1µm)
24, 54	In-House	• Dicyclohexyl Phthalate	• Acetone + 0.1% Trifluoroacetic Acid	• Dilute • 10 minute sonication • Filter	*Splitless:* 150°C *Split:* Ratio: 25:1 Temp: 300°C	*Gradient:* Initial Temp: 150°C Final Temp: 280°C *Isothermal:* 225°C	FID	HP-50+ (30m x 0.53mm x 1.5µm) DB-1MS (30m x 0.25mm x 0.25µm)
6, 27, 58	• In-House • Manufacturer method	• None • Dicyclohexyl Phthalate	• Hexane/Acetone	• Dilute • 15-30 minute sonication • 10-30 minute shake • Filter	*Split:* Ratio: 2:1 to 100:1 Temp: 250-275°C	*Gradient:* Initial Temp: 200°C Final Temp: 280°C *Isothermal:* 210-260°C	FID	DB-1 (15m x 0.25mm x 0.25µm) HP-1 (30m x 0.25mm x 0.25µm) HP-5 (30m x 0.32mm x 0.25µm)
40, 88	In-House	• None • Ametryn	• Hexanes	• Dilute • 5-30 minute sonication • 30 minute shake • Filter	*Splitless:* 250°C *Split:* Ratio: 100:1 Temp: 265°C	*Gradient:* Initial Temp: 60-150°C Final Temp: 280-320°C	ECD MSD	HP-5 (30m x 0.32mm x 0.25µm) BP-5MS (20m x 0.18mm x 0.18µm)

Table 13: Representative LC Methods for the determination of Lambda-Cyhalothrin

Lab #	Reference Methods	Extractants	Sample Preparation	Mobile Phase	Detector	Wavelength (nm) or MRM Transition (m/z)	Column
44, 102	• In-House	Acetonitrile	• Dilute • 10-20 minute sonication • Filter	A: 5mM Ammonium Formate + 0.1% Formic Acid in Water (or 1% Formic Acid in Water) B: 5mM Ammonium Formate + 0.1% Formic Acid in 90% Methanol (or 1% Formic Acid in Methanol)	MSD	467 > 225 467 > 141 450.1 > 225.2 450.1 > 141.1	Acquity HSS T3 (8µ, 2.1x100mm) Acquity BEH C18 (1.7µ, 2.1x50mm)
9, 16, 68, 71, 76, 91, 107, 109	• In-House • Manufacturer method	85-100% Acetonitrile 0-15% Water	• Dilute • 10-60 minute sonication • Cool • Filter	A: Water B: Acetonitrile	FID	230 235 252 254 260	Kinetex EVO C18 (5µ, 4.6x150mm) ODS C18 (5µ, 4.6x250mm) Chromanik C18 (5µ, 4.6x250) Eclipse Plus C18 (3.5µ, 4.6x100mm) ACE C18 (5µm, 4.6x250mm)
22, 23, 25, 39, 58	• In-House • Manufacturer method	Methanol	• Dilute • 30 minute sonication o 30 second vortex • 30 minute shake • Filter	A: Water (or 0.05-1% Phosphoric Acid) (or 3% Acetic Acid) B: Methanol (or Acetonitrile)	FID	212 235 280	Discovery C18 (5µ, 4.6x250mm) Partisphere RTF C18 (5µ, 4.6x250mm) LiChrosorb RP-18 (5µ, 4.6x200mm) Eclipse XDB-C8 (5µ, 4.6x150mm) Zorbax SB-C18 (5µ, 4.6x250mm)
37	• In-House	Acetone	• Dilute • 1 hour stirring • Filter	A: 60-10% Water (gradient) B: 40-90% Acetonitrile (gradient)	FID	225	Zorbax SB-C18 (5µ, 4.6x150mm)
45, 47	• Manufacturer method	Acetonitrile + 0.1% Trifluoroacetic Acid	• Grind sample • 30-60 minute sonication • Filter	A: 0.5% Acetic Acid in Water B: Acetonitrile (or Methanol)	FID	275	Luna C18(2) (5µ, 4.6x250mm)
56	• In-House	3% Tetrahydrofuran 97% Acetonitrile	• Dilute • 15 minute shake • Filter	A: Water B: Acetonitrile	FID	280	Alltima Cyano 100A (4.6x250mm)

STATISTICAL ANALYSIS

1. **Robust Mean**
   The purpose of using a robust estimator of the mean was to cope with the possibility of outlying data points without having to remove them from the sample.

   The robust mean estimator used was the median.

2. **Robust Estimate of Standard Deviation**
   The robust estimate of the standard deviation used was the MAD_E value.

   To obtain MAD_E,

   Calculate Median Absolute Deviation (MAD) from the sample median:

   $$MAD = median(|X_i - median(X_i)|_{i=1,2,\ldots,n})$$

   Calculate MAD_E:
   $$MAD_E = K \times MAD$$

   For normally distributed data, $K \approx 1.483$.

   $$MAD_E = 1.483 \times MAD$$

3. **Calculation of Modified Z-scores**
   Modified Z-scores (Z_i) for each laboratory were calculated as:

   $$Z_i = 0.6745 \times (X_i - median)/MAD$$

   Z values falling outside the range of $-3.5 \leq Z_i \leq 3.5$ were marked as outliers.

4. **Presentation of Data**
   Data is presented graphically in two ways:

   i. A scatter plot showing each participating laboratory's two-day mean value for each analyte along with the associated standard deviation. These plots also show the upper and lower Horwitz limits for the sample, as well as the median ± 2 MAD_E .

   ii. A plot of modified Z-scores.

5. **References**

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   iii. Fallon, A., Spada , C., Detection and Accommodation of Outliers in Normally Distributed Data Sets, Virginia Polytechnic Institute and State University, *http://www.webapps.cee.vt.edu/ewr/environmental/teach/smprimer/outlier/outlier.html* (Accessed: 03/13/2013)